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STUDIES OF ATMOSPHERIC PROCESSES

Frederick P. Boynton, et al

Wayne State University

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by

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Detroit, Michigan 48202

Contract No. F19628-72-C-0007

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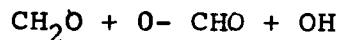
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## 13. ABSTRACT

The research described in this report is aimed at characterizing the non-equilibrium flow and coupled chemistry associated with the interaction of rocket exhaust effluents in the upper atmosphere. Infrared chemiluminescence emitted from the reaction between O and  $C_2H_4$  has been quantitatively measured under lean conditions. The ratio of the rate coefficients for the reactions



is found to be 1.7 while the rate coefficient for the reaction



is found to be less than  $3 \times 10^{-14}$  cc/sec with a quantum yield of less than 20%.

A compilation of all available cross section information is included herein for use in highly rarefied plume calculations.

The molecular beam measurements on the interaction potential between O atoms and plume species is described.

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## ABSTRACT

The research described in this report is aimed at characterizing the non-equilibrium flow and coupled chemistry associated with the interaction of rocket exhaust effluents in the upper atmosphere. Infrared chemiluminescence emitted from the reaction between O and C<sub>2</sub>H<sub>4</sub> has been quantitatively measured under lean conditions. The ratio of the rate coefficients for the reactions



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A compilation of all available cross section information is included herein for use in highly rarefied plume calculations.

The molecular beam measurements on the interaction potential between O atoms and plume species is described.

## PREFACE

The research described in this report falls into four main categories, identified in the contractual work statement as follows:

- a) Calculate the continuum flow structure and rate chemistry of high altitude plumes.
- b) Calculate the vibrational excitation cross-sections for plume relevant species using available interaction potential data.
- c) Measure the quantum yields in the infrared region for the chemi-excitation involving O or OH and plume species.
- d) Measure the inter-molecular potential between atomic oxygen and various plume species as an input to the calculation of vibrational excitation cross sections.

Item (a) is discussed in Section I, item (b) in Section II, item (c) in Section III, and item (d) in Section VI.

## I. Fluid Mechanical Studies

In this portion of the Wayne State effort, emphasis has been focused on two specific problem areas: development of a 1-D unsteady continuum fluid description as a bridge between the 2-D steady continuum MULTITUBE code and a full Monte Carlo rarefied flow description (under development at TRW), and examination of the methodology for including chemistry and excitation processes in a 1-D Monte Carlo rarefied flow description.

The development of the 1-D unsteady continuum flow code has been described in the previous semi-annual technical report dated 15 December, 1971.<sup>(1)</sup> To date the coding on this program has been completed and the calculation successfully checked out for the case of expansion into a vacuum. Current effort is focused on studying shock formation, i.e. studying the development of shock structure through a thick shock description. This phase of the fluid study will be carried on by F. Boynton elsewhere.<sup>(2)</sup>

The Monte Carlo code development has several purposes in addition to accounting for chemistry and excitation processes. These include an examination of multicomponent effects in a simple geometry and as a means of gaining familiarity with the structure of a Monte Carlo analysis for advisory purposes in chemistry input. The early development of the Monte Carlo code is described in the semi-annual report dated 15 December, 1971, so will not be further described here. Work in this last 6 months has established the validity of the 1-D unsteady Monte Carlo code for shock wave formation. A routine for the inclusion of vibrational excitation processes has been developed and included into the M-C analysis. In addition, this excitation subroutine has been forwarded to TRW for inclusion with the full Monte Carlo development underway at TRW. The current problem in the M-C code development is that when the excitation probability is small, the code is slow in running on the IBM 360/67 and CDC 7600 machines.

Literature Cited

- 1) F.P. Boynton, E.R. Fisher, R.H. Kummier and P.K. Rol,  
Semi-Annual Technical Report No.115 December (1971).
- 2) Physical Dynamics, Inc., San Francisco, California.

## II. Vibrational Cross Sections

In the high altitude rarefied flow regime, highly non-thermal collisions characterize the interaction between ambient atmospheric species and exhaust constituents. In order to characterize the excitation processes associated with these high relative energy collisions, cross section information for various plume and atmospheric species must be generated. The close coupling code of Marriott<sup>(1)</sup> has been applied to some of these cross section calculations over the past years. In this reporting period, the results of Marriott's past cross section calculations, in addition to some new results of plume interest, have been correlated into a form convenient for evaluation of the excitation cross section at any collision energy above threshold.

No experimental information is available on the excitation cross sections for any of the collision processes calculated. Therefore, in order to attempt to assess the validity of these cross section calculations, rate coefficients (or relaxation times) have been generated by integrating the cross sections over a Boltzmann distribution of relative energies. Where thermalized data are available these calculated relaxation times have been compared and conclusions drawn.

Table IIIa

State Notation for the Polyatomic Species

<u>Notation</u>	<u>v<sub>1</sub></u>	<u>v<sub>2</sub></u>	<u>v<sub>3</sub></u>
0	0	0	0
1	0	1	0
2	0	2	0
3	1	0	0
4	0	0	1

A full description of the theoretical close coupling code is currently being included in a technical report describing this work<sup>(2)</sup> and is also available elsewhere so only the results will be summarized here. The species considered in this tabulation include CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and He. The state notation for the polyatomic species is given in Table IIa. It should be noted that the v<sub>2</sub> bending mode of CO<sub>2</sub> is doubly degenerate and the cross sections do not account for this, i.e. the total excitation cross section from ground to the v<sub>2</sub> = 1 state is twice the cross section listed (see Marriott for a further discussion of this).

The functional form assumed for correlating the energy dependence of the cross section is

$$\sigma(E) = C_3 \ln(E/E_T) ^{C_2} (E_T/E) ^{C_4} \quad \text{II-1}$$

where E = relative collision energy (eV)

E<sub>T</sub> = threshold energy

and σ(E) = excitation cross section (cm<sup>2</sup>).

Table IIb lists all the coefficients to equation (II-1) for the reactions studied.

These cross section functions can be integrated over a Boltzmann distribution of relative energies, yielding rate coefficients with the inclusion of degeneracy factors. The complete tabulation of rate coefficients as determined from the data in Table IIb will be available in a forthcoming report complete with the comparison to available rate coefficient data.<sup>(2)</sup> The conclusions drawn from these comparisons are, that at high temperatures the agreement between the calculated rate coefficients and measurements is good in all cases for which data exist except CO<sub>2</sub>(v<sub>2</sub>) + H<sub>2</sub>. At lower temperatures, i.e. below 1000°K, the calculated rate coefficients are generally smaller than the data suggest reflecting the neglect of vibration-rotation (VR) and vibration-vibration (VV) processes in the calculation of the cross sections. These latter processes, particularly VR processes, are expected to be important in effecting thermalized energy transfer processes involving H<sub>2</sub> and H<sub>2</sub>O. For the case of CO<sub>2</sub>(v<sub>2</sub>) + H<sub>2</sub>, the calculated

Table II

Coefficients to Cross Section vs. Energy Function

<u>REACTION</u>	<u>ET</u>	<u>C2</u>	<u>C3</u>	<u>C4</u>
N2 + AR Q(01)	2.89E-01	1.093E01	1.110E-23	0.0
CO + HE Q(01)	2.660E-01	3.658E00	3.263E-20	-2.147E00
CO + HE Q(02)	5.310E-01	3.659E00	8.189E-23	-4.857E00
CO + HE Q(12)	2.660E-01	3.779E00	1.299E-19	-8.742E-01
CO + H2O Q(01)	2.660E-01	1.306E01	1.449E-18	3.183E-00
CO + H2O Q(02)	5.310E-01	1.175E01	2.189E-20	1.764E-00
CO + H2O Q(12)	2.660E-01	6.830E00	4.082E-22	-2.357E-00
H2O + H2 Q(01)	1.980E-01	3.937E00	3.755E-16	1.380E-00
H2O + H2 Q(02)	3.950E-01	4.387E00	1.630E-16	1.734E-00
H2O + H2 Q(12)	4.410E-01	2.628E00	2.205E-18	-3.184E-01
H2O + H2 Q(14)	4.650E-01	3.488E00	1.183E-18	4.102E-01
H2O + H2 Q(23)	1.980E-01	2.398E00	1.939E-16	7.175E-01
H2O + H2 Q(24)	2.430E-01	4.588E00	5.263E-17	1.374E-00
H2O + H2 Q(34)	2.680E-01	5.631E00	2.619E-17	1.999E-00
H2O + H2 Q(01)	4.560E-02	3.992E00	5.143E-18	3.068E-01
H2O + H2 Q(02)	7.000E-02	4.180E00	3.589E-18	5.583E-01
H2O + H2 Q(03)	3.440E-02	9.229E00	5.393E-18	2.230E-00
H2O + H2 Q(04)	1.980E-01	5.160E00	2.754E-17	1.287E-00
H2O + H2 Q(12)	3.950E-01	3.355E00	8.759E-19	-3.844E-01
H2O + H2 Q(13)	4.410E-01	3.260E00	5.112E-20	1.400E-00
H2O + H2 Q(14)	4.650E-01	3.134E00	2.065E-20	1.100E-00
H2O + H2 Q(23)	1.980E-01	3.682E01	1.676E-18	-1.709E-00
H2O + H2 Q(24)	2.430E-01	3.977E00	2.756E-17	1.144E-00
H2O + H2 Q(34)	2.680E-01	3.728E00	5.328E-18	9.232E-01
H2O + CO2 Q(01)	4.560E-02	6.307E00	1.993E-16	2.017E-00
H2O + CO2 Q(02)	7.000E-02	5.153E00	1.067E-16	1.835E-00
H2O + CO2 Q(03)	2.440E-02	1.157E00	1.419E-16	2.017E-01
H2O + CO2 Q(04)	1.980E-01	1.098E01	1.708E-19	1.569E-00
H2O + CO2 Q(12)	3.950E-01	8.663E00	9.932E-21	6.524E-02
H2O + CO2 Q(13)	4.410E-01	1.481E01	1.103E-19	4.090E-00
H2O + CO2 Q(14)	4.650E-01	5.116E00	1.689E-23	3.680E-00
H2O + CO2 Q(23)	1.980E-01	4.923E00	3.386E-19	3.393E-01
H2O + CO2 Q(24)	2.430E-01	2.119E01	1.793E-16	8.457E-00
H2O + CO2 Q(34)	2.680E-01	1.451E01	9.282E-18	5.192E-00
H2O + CO2 Q(01)	4.560E-02	8.291E00	2.392E-17	1.948E-00
H2O + CO2 Q(02)	7.000E-02	7.518E00	5.091E-17	2.180E-00
H2O + CO2 Q(03)	2.440E-02	4.117E00	1.289E-16	9.704E-01
H2O + CO2 Q(04)	8.280E-02	3.748E00	4.420E-16	1.244E-00
CO2 + H2 Q(01)	1.660E-01	2.133E00	1.142E-16	3.772E-01
CO2 + H2 Q(02)	1.640E-01	4.145E00	9.133E-17	1.176E-00
CO2 + H2 Q(03)	2.910E-01	5.473E00	2.600E-17	1.721E-00

Table con't.

<u>REACTION</u>	<u>ET</u>	<u>C2</u>	<u>C3</u>	<u>C4</u>
CO2 + H2 Q(12)	8.280E-02	2.267E00	8.757E-16	9.479E-01
CO2 + H2 Q(13)	8.090E-02	1.395E00	2.359E-17	4.906E-02
CO2 + H2 Q(14)	2.090E-01	3.476E00	5.288E-18	4.379E-01
CO2 + H2 Q(32)	2.000E-03	5.107E01	8.254E-38	7.115E-00
CO2 + H2 Q(24)	1.260E-01	7.104E00	9.580E-18	1.683E-00
CO2 + H2 Q(34)	1.280E-01	4.391E00	5.831E-18	3.820E-01
CO2 + H2O Q(01)	8.280E-02	4.693E00	1.256E-16	1.173E-00
CO2 + H2O Q(02)	1.660E-01	5.237E00	2.408E-17	1.217E-00
CO2 + H2O Q(03)	1.640E-01	4.624E00	1.387E-18	2.679E-01
CO2 + H2O Q(04)	2.910E-01	4.696E00	1.870E-20	-1.638E-00
CO2 + H2O Q(12)	8.280E-02	6.947E00	5.245E-17	1.795E-00
CO2 + H2O Q(13)	8.090E-02	6.495E00	8.598E-18	1.726E-00
CO2 + H2O Q(14)	2.090E-01	1.164E01	7.792E-16	5.282E-00
CO2 + H2O Q(32)	2.000E-03	1.030E01	6.608E-21	1.440E-00
CO2 + H2O Q(24)	1.260E-01	1.488E01	1.483E-15	6.078E-00
CO2 + H2O Q(34)	1.280E-01	4.601E00	9.341E-19	-4.290E-01
CO2 + CO2 Q(01)	8.280E-02	1.955E01	4.993E-19	4.957E-00
CO2 + CO2 Q(02)	1.660E-01	1.144E01	3.059E-20	1.324E-00
CO2 + CO2 Q(03)	1.640E-01	1.530E01	4.223E-20	3.533E-00
CO2 + CO2 Q(04)	2.910E-01	1.926E01	1.209E-17	7.240E-00
CO2 + CO2 Q(12)	8.280E-02	2.804E00	4.183E-18	0.0
CO2 + CO2 Q(13)	8.090E-02	1.064E01	2.919E-19	2.411E-00
CO2 + CO2 Q(14)	2.090E-01	2.067E01	1.880E-15	8.969E-00
CO2 + CO2 Q(32)	2.000E-03	1.048E00	2.062E-17	0.0
CO2 + CO2 Q(24)	1.260E-01	1.968E01	7.164E-16	7.333E-00
CO2 + CO2 Q(34)	1.280E-01	8.858E00	6.543E-20	2.766E-01

results are larger than measurements suggest even without the inclusion of VR processes. Apparently, this can only be interpreted by assuming that the interaction potential used in the calculation is not quite correct. This point is being currently investigated.

In summary, the cross section information listed in Table II b is the only source of high energy excitation data available for use in the rarified plume - atmosphere chemistry description. These data are expected to be reliable for this application even though the thermalized comparisons show some disagreement with data. This is due to the expectation that at high relative collision energies, VR and VV processes will be relatively unimportant compared to direct VT excitation.

Current work on the close coupling code is aimed at including structure in the collision partner in order to characterize VV processes for species of plume interest.

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R. Marriott, RIES Report 70-17 (1970).
- (2) E.R. Fisher, "Vibrational Excitation Cross Sections and Rate Coefficients for VT Processes Involving CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and CO," report in preparation.

### III. Flow Discharge System Measurements

Prior to quantitative model predictions on the radiative properties of exhaust products in the upper atmosphere, several important chemical reaction rate coefficients must be determined. In particular, our studies have focussed on simple exothermic oxidation reactions involving O and OH attack on various hydrocarbon fuel species and accompanying vibrational relaxation processes.

The interest simple exothermic reactions is directed toward the release of the available energy of the reaction into radiative modes of the product molecules. Measurements in our laboratory have been made from 2500 Å to 25 μ in an attempt to determine the reaction mechanism and available radiative modes.

In order to determine which of the various hydrocarbon reactions was worth studying in detail, i.e. determining quantum yields at 2.7 μ, a brief review of hydrocarbon combustion chemistry was performed. A simplified flow diagram for the decomposition of straight chain hydrocarbons is shown in Fig. III a. We note that O atom attack on  $C_nH_{2n+2}$  produces OH in a nearly thermoneutral reaction in addition to the  $C_nH_{2n+1}$  radical. This radical is rapidly attacked by O atoms to produce  $C_nH_{2n}$  and OH with sufficient exothermicity to produce vibrationally excited OH\*.  $H_2O^*$  can subsequently be produced by the reaction OH + OH. This cycle continues, as outlined in the figure until  $C_2H_4$  is formed. This then decomposes as shown in Fig. VIb upon further O atom attack.

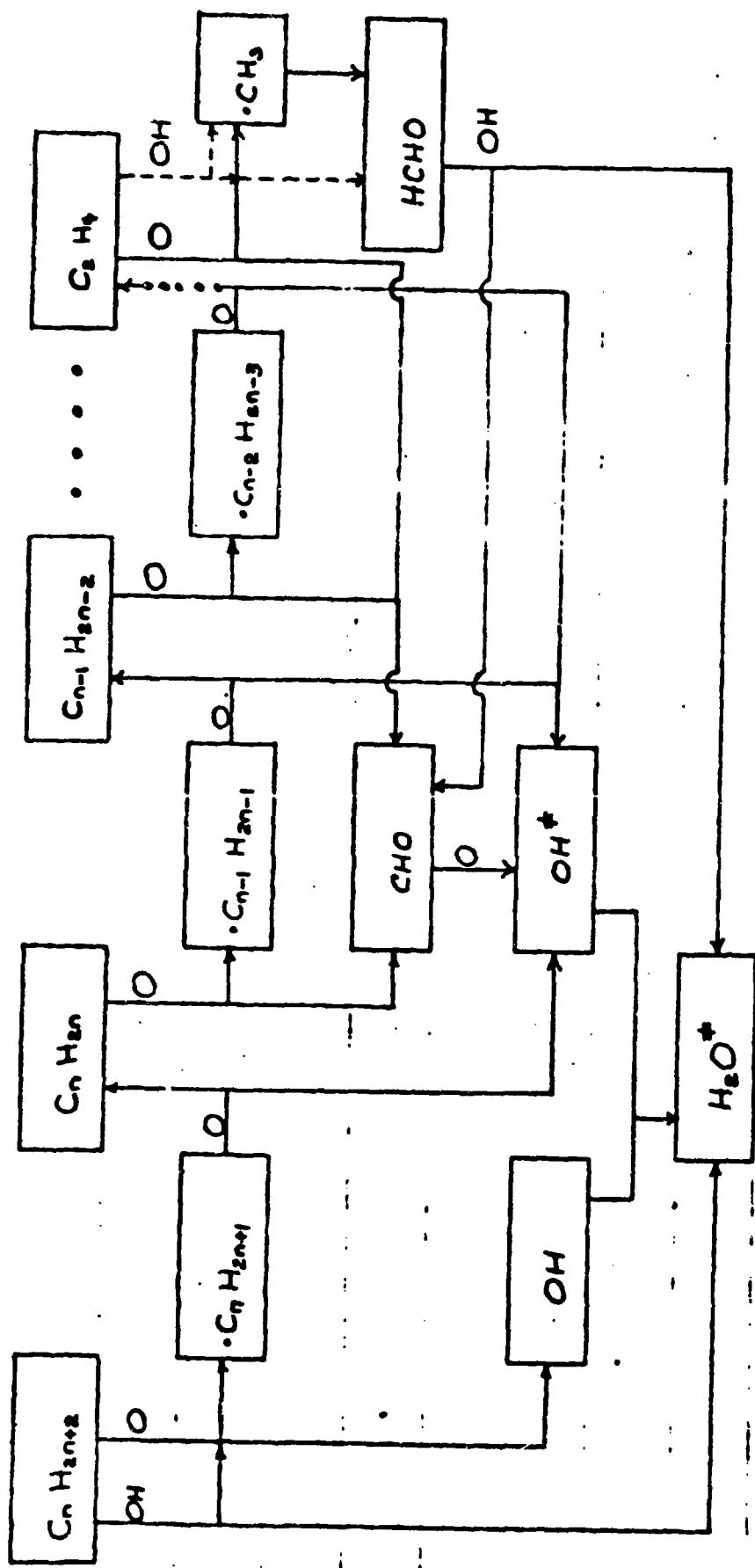


FIGURE IIIa. SIMPLIFIED FLOW DIAGRAM FOR LOW TEMPERATURE STRAIGHT CHAIN HYDROCARBON COMBUSTION. ACTUAL PROCESS WILL ALSO FORM HIGHER ALDEHYDES, EPOXIDES, ETC. AND WILL FORM FRAGMENTS AT THE DOUBLE BOND.

OXYGEN ATOM ATTACK ON ETHYLENE

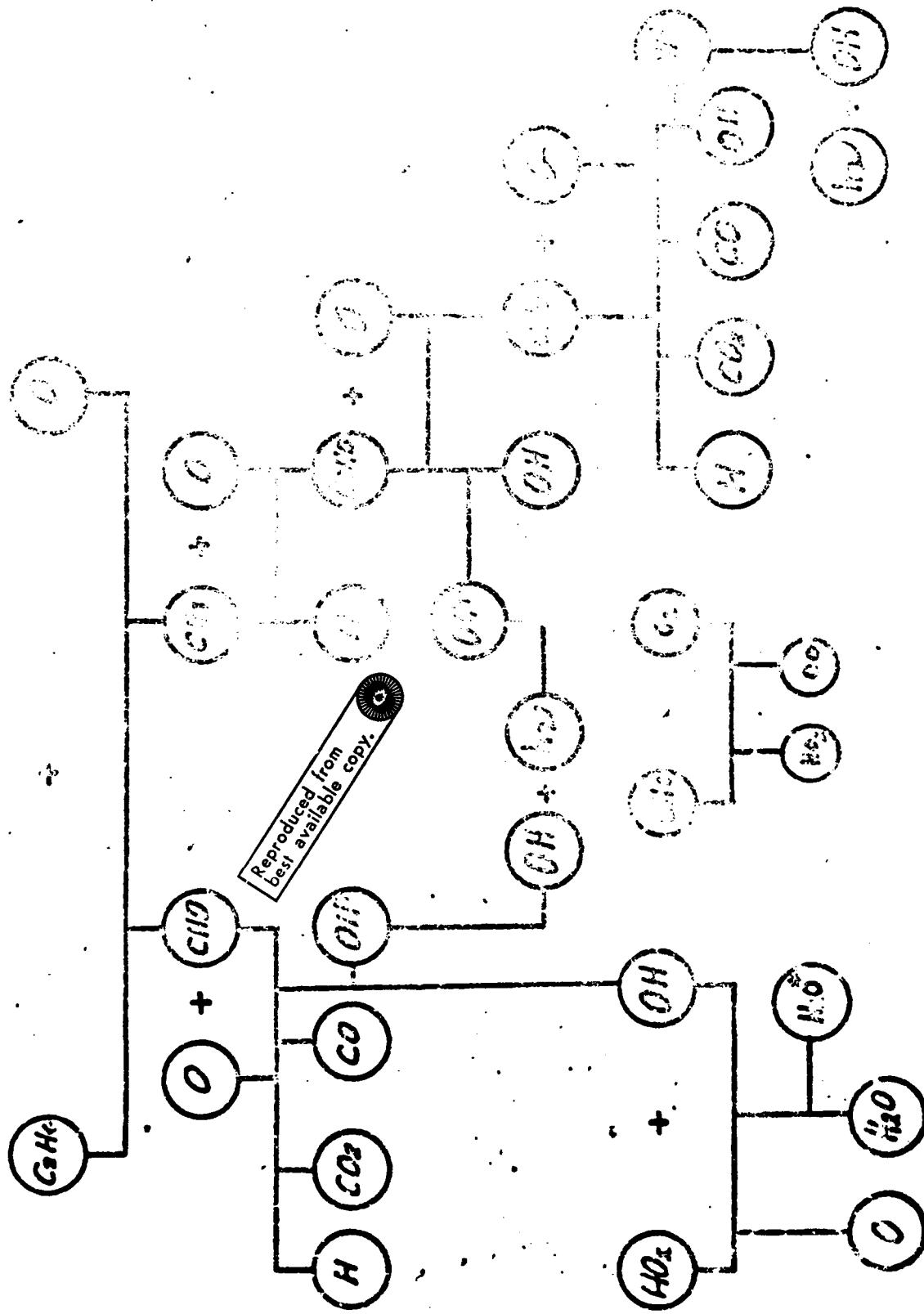
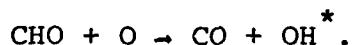


Figure IIfb. Schematic of the Reaction Mechanism Proposed

The attack of O atoms on  $C_2H_4$  has been selected as a prototype reaction in the degradation of straight chain hydrocarbons by O atoms. From Figure IIIb, the primary products are  $CHO + CH_3$ . The rapid reaction of  $O + CHO$  is sufficiently exothermic to produce  $OH^*$ . At low concentrations of  $C_2H_4$ ,  $OH^*$  is expected to be the dominant  $2.7\mu$  radiator. This is discussed at length in a recent thesis performed at Wayne State University under the direction of R. Kummeler.<sup>(1)</sup> The work performed during that thesis study will be published as a technical report under the plume program.

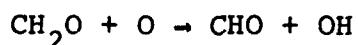
To summarize the results of that study, experimental infrared measurements at  $2.7\mu$  were taken for the reaction system illustrated in Figure IIIb at low concentrations of  $C_2H_4$ . Under these conditions, as shown in the computer simulation of Figure IIIc, the  $OH^*$  is considerably higher in concentration than  $H_2O^*$  (both of which radiate at  $2.7\mu$ ). The kinetic mechanism in the computer model is shown in Table IIIa. Under these lean conditions, strong  $2.7\mu$  emission is observed from the primary radiation step



The primary CHO loss step is found to be the reaction



The ratio of rate coefficients for these two competitive CHO reactions is experimentally found to be 1.7.<sup>(1)</sup> In addition, the rate coefficient for the slightly exothermic reaction



is found to be less than  $3 \times 10^{-14}$  cc/sec with a quantum yield of less than 20%.<sup>(1)</sup> A full report of this study is being prepared.

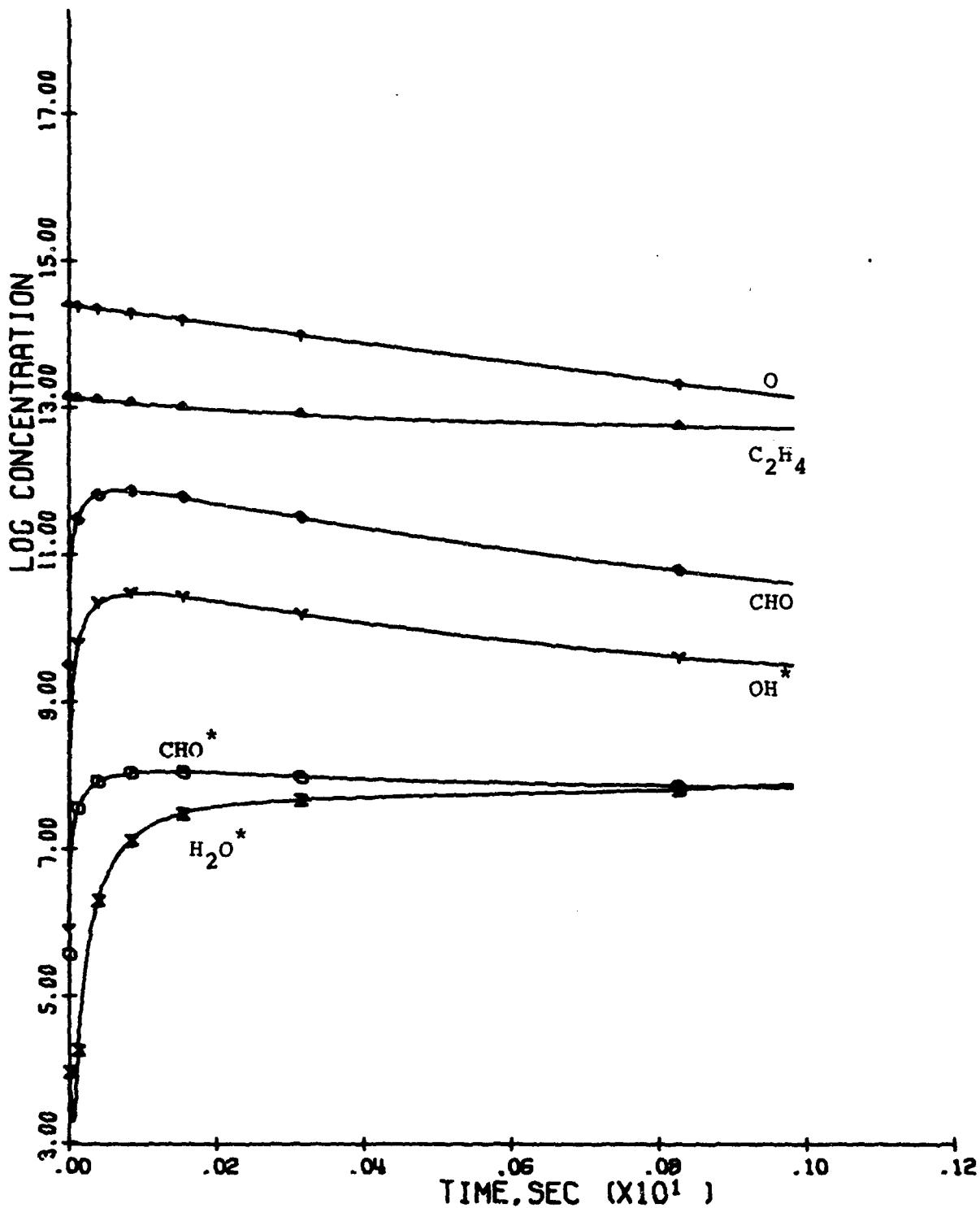


Figure IIIb. Computer simulated concentration profiles in the flow discharge system.

KINETICS OF THE REACTIONS.  
TIME = 3.65499E-03 SEC.

NO.		REACTION		CONSTANT	RATE
1.	C2H4 + O	=CH3 + CHO		8.4E-13	6.0E 14
3.	HCHO + O	=CHO + OH <sup>+</sup>		3.0E-15	1.3E 12
5.	CHO + O	=CO <sub>2</sub> + H		3.0E-14	7.4E 11
7.	CHO + H	=CO + H <sub>2</sub>		4.0E-12	1.1E 13
9.	CHO + O <sub>2</sub>	=CO + HO <sub>2</sub>		1.0E-12	6.9E 14
11.	OH + OH	=H <sub>2</sub> O + O		2.5E-12	1.1E 11
13.	CH <sub>3</sub> + O <sub>2</sub> + M	=CH <sub>3</sub> O <sub>2</sub> + M		8.0E-32	1.6E 12
15.	H <sub>2</sub> O <sup>+</sup> + M	=H <sub>2</sub> O + M		1.0E-12	1.7E 12
17.	HCHO + O	=CHC + OH		6.0E-14	2.6E 13
19.	OH + HCHO	=H <sub>2</sub> O + CHC		1.4E-11	1.5E 13
21.	OH + H <sub>2</sub>	=H <sub>2</sub> O + H		6.6E-15	5.2E 07
23.	H <sub>2</sub> O <sub>2</sub> + O	=OH + O <sub>2</sub>		1.0E-11	6.9E 14
25.	OH + HO <sub>2</sub>	= H <sub>2</sub> O <sup>+</sup> + O <sub>2</sub>		1.0E-12	1.7E 11
27.	CHO* + O	=CO + OH <sup>+</sup>		1.0E-11	8.0E 10
29.	O + HO <sub>2</sub>	=OH <sup>+</sup> + O <sub>2</sub>		3.0E-14	2.1E 12
31.	CH <sub>3</sub> O <sub>2</sub> + HV	=CH <sub>3</sub> O <sub>2</sub> + HV		1.0E-20	7.3E-11

NO.		REACTION		CONSTANT	RATE
2.	CH <sub>3</sub> + O	=HCHO + H		3.0E-11	6.3E 14
4.	CHO + O	=CO + OH		1.0E-13	2.5E 12
6.	OH + O	=O <sub>2</sub> + H		5.0E-11	9.1E 14
8.	OH <sup>+</sup> + HV	=OH + HV		3.3E 00	4.4E 10
10.	OH <sup>+</sup> + O	=OH + O		5.0E-11	5.7E 13
12.	OH + OH	= H <sub>2</sub> O <sup>+</sup> + O		2.5E-13	1.1E 10
14.	H + O <sub>2</sub> + M	=HO <sub>2</sub> + M		3.0E-32	2.4E 13
16.	H <sub>2</sub> O <sup>+</sup> + HV	=H <sub>2</sub> O + HV		3.5E 01	1.7E 09
18.	CHO + O	=CO + OH <sup>+</sup>		2.0E-12	4.9E 13
20.	OH + HCHO	= H <sub>2</sub> O <sup>+</sup> + CHO		1.4E-12	1.5E 12
22.	OH + HO <sub>2</sub>	=H <sub>2</sub> O + O <sub>2</sub>		1.0E-11	1.7E 12
24.	H + HO <sub>2</sub>	=OH <sup>+</sup> + OH		3.0E-15	2.3E 10
26.	C2H4 + O	=CH3 + CHO*		1.0E-16	7.2E 10
28.	H + HO <sub>2</sub>	=OH + OH		1.0E-11	7.7E 13
30.	CO + OH	=CO <sub>2</sub> + H		1.5E-13	1.7E 11
32.	H <sub>2</sub> O + CO <sub>2</sub>	=H <sub>2</sub> O + CO <sub>2</sub>		1.0E-20	4.2E 00

Figure IIIa. Kinetic reactions and rate coefficients at 300°K for the computer (Simulation of Figure IIIb).

## Experimental

All studies were performed in the discharge flow system shown schematically in Figure IIId. Molecular oxygen (American Cryogenics, purity 99.6%) was discharged in an Evenson or Broida Cavity at 2450 MHZ using a Raytheon PGM 10x2 diathermy system. The discharge was pulsed at 238 Hz for simultaneous infrared, visible and ultraviolet measurements. The discharged oxygen was passed into the flow tube reactor through a teflon tube with a radially-multiperforated exit stream which permits excellent mixing with a second gas and prevents discharge region radiation from reaching the observation ports. The stainless steel reactor is lined with a teflon sleeve which largely prevents wall recombination of the atomic species. The inside diameter of the reactor is one inch and typical gas velocities are 30 to 40 m/sec through a Heraeus Engelhard E - 225 mechanical pump. Six ports permit radial viewing through KBr windows using an RCA C31025C uncooled photomultiplier on a Jarrell Ash scanning quarter meter monochrometer with a Keithley 602 Electrometer recorded on a Honeywell Electronik 194 recorder. Signal to noise ratios were such that no damping or time integration of signals was necessary in the u.v. and visible. Measurements in the infrared were made using a Santa Barbara uncooled PbS detector (to  $3\mu$ ), Ge:Au detector (to  $8\mu$ ) and Ge:Cu detector (to  $25\mu$ ). All infrared measurements were made with a PAR HR8 Phase Sensitive Lock in Amplifier.

The hydrocarbons employed as reactant gases were methane, ethane, propane, ethylene, propylene, trans-butene, acetylene and formaldehyde. Linde research grade methane and ethane were employed. Union Carbide chemically pure propane was used. The propylene and trans-butene from Cryogenic Sales had purities of 95% and 99% respectively. Several runs were made with "house" methane with no perceptibly different results.

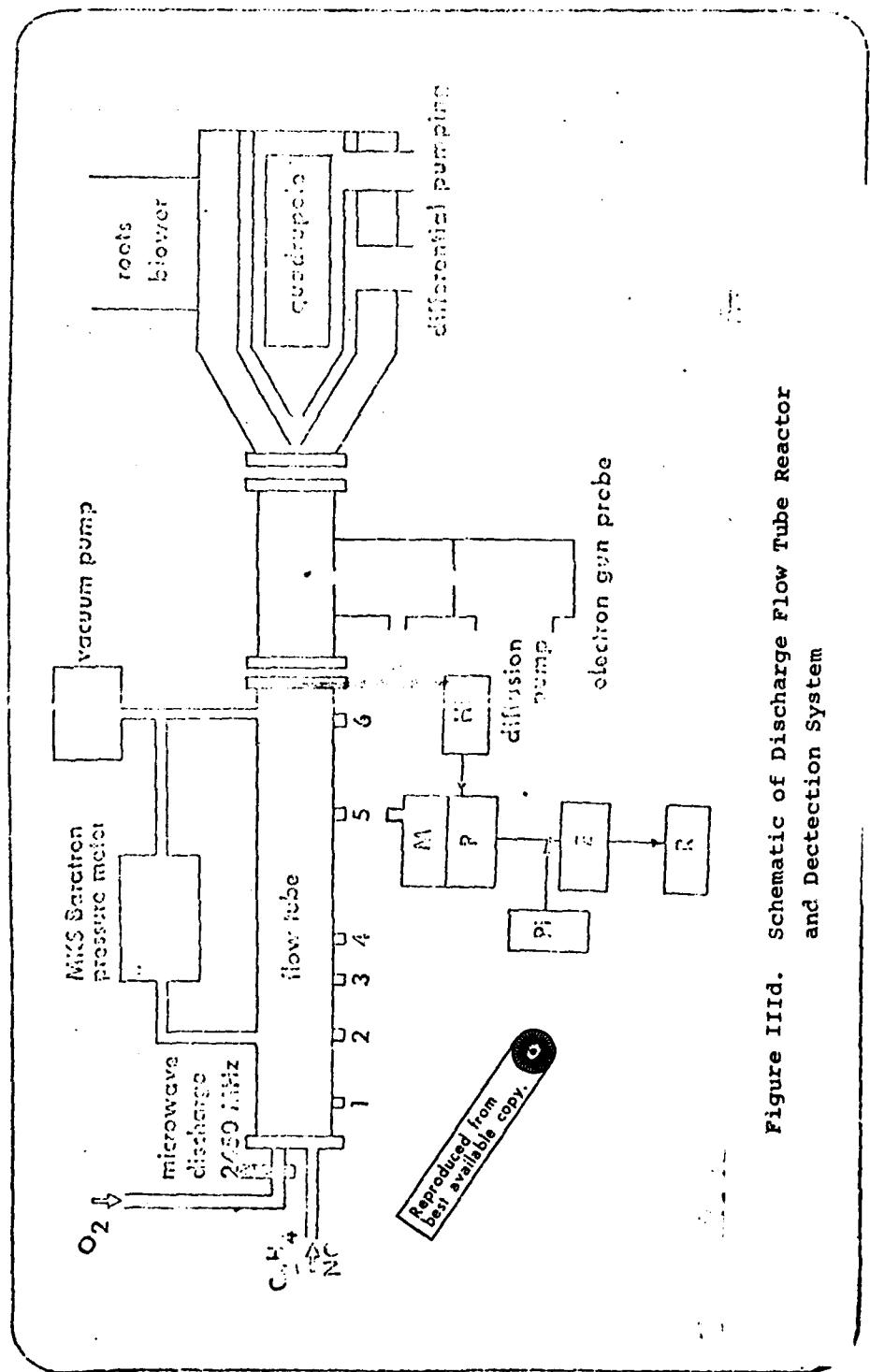


Figure IIId. Schematic of Discharge Flow Tube Reactor  
and Detection System

**Figure IIId.** Schematic of discharge flow tube reactor  
and detection system. Legend:

M = Monochromator - Jarrell Ash, quarter meter,  
scanning.

P = Photomultiplier - RCA C31025C (uncooled).

E = Electrometer, D.C. Amplifier - Keithley 602.

Pi = Picoampere source - Keithley 602.

R = Recorder - Honeywell Electronik 194.

Hi = High voltage C.C. power supply - Power  
Designs Pacific model 2K-10.

### Summary of Wayne State Measurements

A summary review of all the flow discharge measurements to date is presented in Table IIIb. It should be mentioned that reaction (1) in the table is the generation reaction for producing OH, and therefore the reactions initiated with OH, i.e. reactions (2), (3), and (4), have IR signals in excess of reaction (1). Some of these preliminary survey measurements are being further quantified in a way similar to the work on  $O + C_2H_4$ .

Table IIIb. Wayne State University: Summary of Data to June 1972

CHEMILUMINESCENT FLOW TUBE MEASUREMENTS

<u>Reaction System</u>	<u>Visible</u>	<u>2.7<math>\mu</math></u>	<u>5-10<math>\mu</math></u>	<u>Comments</u>
1. H + NO <sub>2</sub> → NO + OH (OH + H <sub>2</sub> → H <sub>2</sub> O + H OH + OH → H <sub>2</sub> O + O)	Meinel bands	large signal	large signal	maximum found in 2.7 $\mu$ signal, no maximum in 5-10 $\mu$
2. OH + CO	nothing	nothing	?	
3. OH + CH <sub>2</sub> O	?	large signal	medium signal	signals greater than (1) above
4. OH + C <sub>2</sub> H <sub>2</sub>	nothing	small signal	medium signal	
5. O + C <sub>2</sub> H <sub>4</sub>	Meinel bands	large signal	medium signal	maximum found in 2.7 $\mu$ signal
6. O + C <sub>4</sub> H <sub>8</sub>	Meinel bands	large signal	?	
7. O + C <sub>3</sub> H <sub>6</sub>	Meinel bands	?	?	
8. O + CH <sub>2</sub> O	Meinel bands (3500-4500 continuum)	large signal	?	maximum found in 2.7 $\mu$ signal
9. O + C <sub>2</sub> H <sub>2</sub>	Meinel bands	small signal	?	
10. O + C <sub>2</sub> H <sub>6</sub>	Meinel bands			
11. O + C <sub>n</sub> H <sub>2n+2</sub>	Meinel bands			
12. O + NH <sub>3</sub>	HNO*			

Literature Cited

(1) M. Malki, "Infrared Chemiluminescence from the Reaction of Oxygen Atoms on Ethylene", MS Thesis, Wayne State University, June (1972).

#### IV. Molecular Beam Experiments

The calculation or measurement of the excitation of exhaust species by atmospheric O atoms is recognized as an important problem. To date, direct experimental measurement of these excitation cross sections has not proved feasible. In this study, the excitation cross sections are calculated using the close coupled code and the intermolecular potential acting between O atoms and plume species. This potential is being experimentally measured using an Amdur-type molecular beam apparatus.

This experiment proceeds by measuring the attenuation of a fast (50 - 5000eV) O atom beam in passing through a scattering gas. The elastic scattering cross section is then determined from

$$\ln(I/I_0) = -nS\ell \quad (\text{VII.1})$$

where  $I$  = attenuated beam flux

$I_0$  = incident beam flux

$n$  = scattering gas density

$\ell$  = path length in scattering gas

and  $S$  = incomplete scattering cross section.

Thus, from a plot of  $\ln(I/I_0)$  vs.  $n$  for a constant  $\ell$ , the cross section can be determined. For a mixture of 2 atomic species in the incident beam, i.e.,  $O(3P)$  and  $O(^1D)$ , the  $(I/I_0)$  vs.  $n$  curve can be resolved into two linear parts, yielding two cross sections.  $S$  is an incomplete cross section since the finite width of the detector and the atomic beam cause part of the scattered particles to reach the detector.

The molecular beam apparatus used in this experiment is shown in Figure IV a. Oxygen atomic ions are produced in the duo-plasmatron source, focused and accelerated through a magnet to separate out both neutrals and molecular ions. The oxygen atomic ion beam is then collimated and energy selected prior to being neutralized by charge exchange with water vapor. The neutralized oxygen atomic

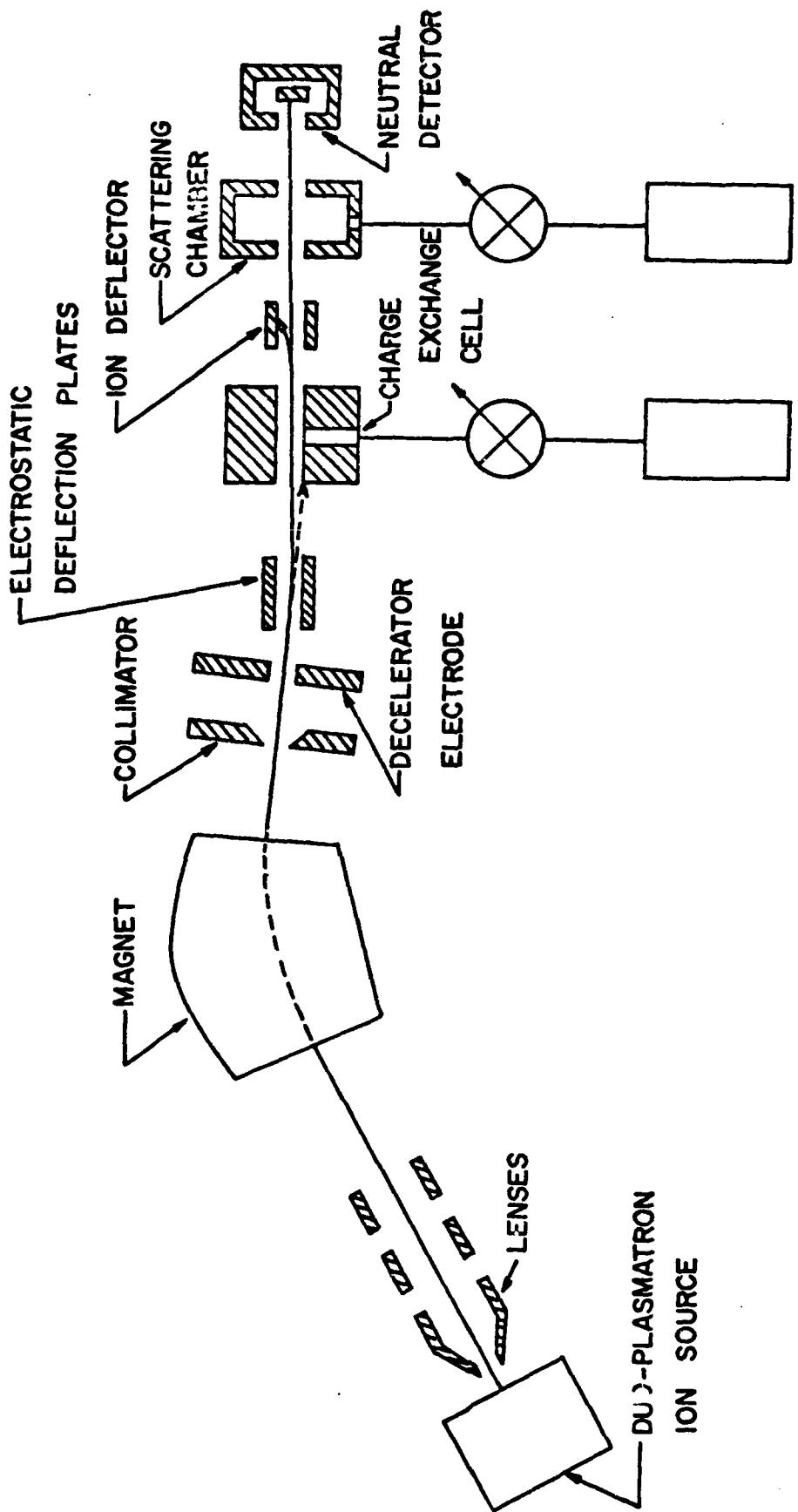


Figure Iva. Amdur-type molecular beam apparatus at Wayne State.

beam is then passed through the scattering chamber and the attenuation measured.

The beam apparatus, donated to Wayne State by NASA, originally had problems with the beam handling system. The original uni-potential lens was replaced by a series of lenses and two sets of deflection plates to guide the beam through the small orifices in the scattering chamber. The system now is operational and preliminary measurements should be available within the month.

Measured incomplete scattering cross sections depend critically on the beam geometry. This fact, not initially recognized in the MIT experiments, is displayed in Figure IV b. Measurements made too close to the cusp in the scattering cross section can yield large errors to the sensitivity in the cross section to variations in both the beam width ( $d$ ) and the detector width ( $\sigma$ ). The potential determined for the case in the figure is  $V(R) = K/r^{2.5}$ .

The repulsive part of the interaction potential determined from these beam experiments is in the range from 1eV to about 30eV. No difficulties are currently anticipated in these measurements.

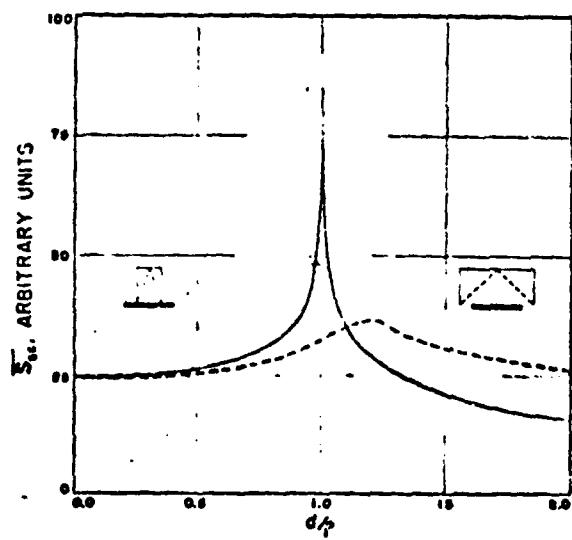


Figure IVb: Calculated dependence of relative beam width ( $d$ ) to detector width ( $p$ ) on scattering cross section.

## V. Rotational Excitation

The rotational excitation of simple molecules plays a critical role in determining the spectral spread of near infrared emission from vibrationally excited molecules. Therefore, a review of rotational excitation models was undertaken to provide background in estimating the spectral signature expected from vibrational emission of CO, CO<sub>2</sub> and H<sub>2</sub>O in non-equilibrium flow environments. This review has been compiled into a report which is in the final stages of typing.<sup>(1)</sup>

In addition, based on this review of rotational excitation processes, short numerical codes have been written to calculate the effective rotational relaxation times of simple molecules, the population distribution of rotational states under non-equilibrium conditions and collision-limited steady state emission from rotational states. The codes are based on Miller's statistical model of rotational excitation<sup>(2)</sup> and employ the rigid rotor approximation.

Literature Cited

- (1) F.P. Boynton, "Recent Developments in Theories of Rotational Excitation of Simple Molecules", report in preparation.
- (2) W.H. Miller, J. Chem. Phys. 52, 543 (1970).

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PREVIOUS CONTRACT AND REPORTS

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"Numerical Calculations of Viscous High-Altitude Exhaust Plume Flow Fields," F.P. Boynton, RIES-70-18.

"Transport Coefficients and Rates of Collisional Energy Transfer of Electrons and Ions in the Upper Atmosphere," A.R. Hochstim, RIES-70-8.

"Quasi-Steady Motions of Weakly Ionized Inhomogeneous Plasma Clouds in a Strong Magnetic Field," J.Alex Thomson, RIES-70-2.

"Energy Deposition in Artificial Ionospheric Heating Experiments," J. A. Thomson, J. Geoph. Res. 75, 6446 (1970), RIES-70-4.

"A Calculation of the Vibrational Excitation of Carbon Monoxide by Collision with Atomic Oxygen in the  $^1D$  State", R. Marriott, RIES-70-17.

"Relaxation Processes in Expanding Flows of Combustion Products," F.P. Boynton and E.R. Fisher, RIES-71-32.

"A Hydrodynamic Analog of Ionospheric Plasma," J. Alex Thomson, invited paper presented at the Fall Meeting of the A.G.U., San Francisco, December 1971.

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